# Hydrodechlorination of Trichloroethylene over Palladium Supported on High Temperature Treated Swellable Organically Modified Silica

Honors Research Distinction Thesis

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Trevor Wendt

Heterogeneous Catalysis Research Group

Dr. Umit Ozkan

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# Abstract

As many parts of the world face water shortages, it is essential to find ways to decontaminate groundwater contaminants like the volatile compound trichloroethylene (TCE). A hydrodechlorination (HDC) reaction could treat this carcinogen by reducing the chlorinated hydrocarbon with hydrogen over palladium metal to produce ethane gas and hydrochloric acid. In order to protect the active metal from anionic poisons like chlorine and sulfur present in groundwater, a novel compound called swellable organically modified silica (SOMS) has been proposed as a possible catalytic support due to its hydrophobicity. However, SOMS is not thermally stable and cannot be used in reactions requiring high operating temperatures. This study examines the effects of fully saturating the material with acetone and calcining it instantly at high temperature (H-SOMS) prior to impregnating palladium catalyst to improve the thermal stability. In order to understand the chemical and physical properties of the H-SOMS, nitrogen physisorption, temperature programmed decomposition (TPD), and CO chemisorption were utilized. The steady-state gas-phase HDC of TCE catalytic activity experiments were performed in a fixed-bed reactor using gas chromatography (GC) to identify and quantify reaction products. These methods showed that the instant heat treatment changed the textual properties of SOMS and increased the accessibility of CO to the Pd sites. The palladium catalyst supported on the H-SOMS did achieve better conversion than original SOMS support (from 38% to 93% at 200ºC). These promising results reveal H-SOMS would make an effective catalytic support for HDC reactions operating at high temperatures. Using this discovery, the cost of water treatment plants could potentially be reduced due to the better utilization and protection of the active metal. Increasing the feasibility of eliminating volatile chlorinated hydrocarbons could result in cleaner and safer drinking water.

# Acknowledgements

My first and most important to thank you goes to Dr. Umit S. Ozkan for her continual support in my pursuit for research. Her expertise and resources have been invaluable for my success for my research project. This thesis would not have been possible without the opportunity to join the Heterogeneous Catalysis Research Group for the past three and a half years. While working in HCRG, I have gained both hard and soft skills, from working with complicated lab equipment and software to gaining an understanding of academia and building relationships with other members. Conducting research in Dr. Ozkan's lab has been one of the most rewarding experiences of my college career.

My graduate student supervisors Hyuntae Sohn and Gokhan Celik have also provided me with countless hours of assistance and guidance during my thesis process. Sohn guided me through my first few years as an HCRG member and helped give me the foundation of knowledge for being able to complete my project. By including me in his own projects, as well as assisting me in completing my own tests, he helped me learn many essential aspects of conducting research and assisted with my success. Gokhan was essential in my final year of research as a helpful mentor during my thesis writing. He kindly involved me in his own projects so my perspective could be expanded and gave me invaluable advice about my research, about graduate school, and life in general. Both of these HCRG members have helped me develop into the chemical engineer I have become today, which I am extremely grateful for.

Finally, I would like to thank my friends and family for their unconditional support. Through long nights of analyzing data and writing, they have always stood by my side and given me encouragement. My parents have been especially helpful in providing me the support I needed to stay motivated to work hard and achieve academic and professional success.

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# Nomenclature

BET = Brunauer-Emmett-Teller Isotherm

BJH = Brunauer-Joyner-Helena Isotherm

BTEB = Bis(trimethoxysilylethyl)benzene

Cu = Copper

FID = Flame Ionization Detector

GC = Gas Chromatograph

H-SOMS = Heat-Treated Swellable Organically Modified Silica

HDC = Hydrodechlorination

IWI = Incipient Wetness Impregnation

Mg = Magnesium

Pd = Palladium

Pt = Platinum

PDHID = Pulsed Discharge Helium Ionization Detector

SOMS = Swellable Organically Modified Silica

TCE = Trichloroethylene

TPD = Temperature-programmed desorption

VOC = Volatile Organic Compounds

# 1. Introduction

Groundwater is an essential source for fresh water for residential, agricultural, and industrial use, and has recently become even more valuable with water shortages becoming more common [1]. However, volatile organic compounds like trichloroethylene can contaminate this water source. Trichloroethylene – a compound containing three chlorine atoms and a hydrogen atom covalently bonded to two double bonded carbons – is used extensively as a metal degreaser and dry cleaning agent [2]. The molecule's extensive use has increased how much of it has entered into the natural environment, causing it to become one of the most common contaminants in groundwater [3]. The primary concern for this change in abundance is that the compound is considered a toxic carcinogen for humans, can cause liver and kidney damage, and can lead to reproductive issues [4]. For this reason, the Environmental Protection Agency sets a limit of 5 ppb of TCE to be allowed in drinking water [5]. According to the Agency for Toxic Substances and Disease Registry, however, TCE was identified to be in excess in 17 different locations in Ohio between 1989 and 2009 [6].

Current methods to remove these VOCs include air stripping and activated carbon adsorption. Air stripping involves injecting air into groundwater in order to strip chlorinated compounds out of the water and into air. However, this requires a substantial volume of air and results in a product that still needs remediated to remove the VOCs from the air [7]. For adsorption, vapor phase TCE is captured using activated carbon. Then, the adsorbed contaminants are transferred to a gas stream and sent to be incinerated. Incineration releases carbon dioxide and other compounds that could potentially be worse than the original compounds, while regeneration of the activated carbon is an inefficient and expensive process [8]. Due to the large energy requirement and carbon footprint of these processes, alternative

methods to removing VOCs from ground water could be more environmentally friendly and economical.

Catalytic hydrodechlorination (HDC) is a potential solution to address the issues that current VOC removal processes create. The HDC reaction provides great benefits by converting TCE into hydrocarbons in a one-step process that can be carried out in groundwater in-situ [9]. By using hydrogen gas as a reducing agent and a metal catalyst (typically palladium), the products from HDC of TCE are ethane and hydrochloric acid [10]. The full reaction is given in equation 1.

$$CCl_2CHCl\ (g) + H_2\ (g) \rightarrow C_2H_6\ (g) + HCl\ (g) \qquad \text{Equation 1}$$

The reaction can be performed at room temperature in liquid or in vapor phase. This method produces few harmful by-products and is non-destructive, so the catalyst in the reaction can be reused, as opposed to the activated carbon in the incinerator. Palladium is the most commonly used active-metal because it reacts with a wide variety of groundwater contaminants and produces high conversion of chlorinated hydrocarbons [11]. Therefore, this specific catalyst will be used throughout the investigations.

Industry typically uses alumina ($Al_2O_3$) as a support for the HDC reaction, however, this compound is vulnerable to ionic poisoning from sulfate ions ($SO_4^{2-}$), hydrogen sulfide ($HS^-$) ions, and chlorine ($Cl^-$) ions. Poisoning can change the chemistry of the catalyst by irreversibly adsorbing onto active sites or through oxidizing the catalytic active sites, leading to low catalytic activity and stability [12]. This problem is further complicated since one of the main products of the reaction is HCl, a strong acid containing an ionic poison. The acidity of the product also can cause an accumulation of carbonaceous products that can reduce the catalytic activity in the

reaction [13]. Therefore, a catalytic support that protects the active palladium in our investigations from poisoning effects is desired.

In order to address the deactivation issues of the catalyst, a novel hydrophobic material will be tested. Swellable organically modified silica (SOMS), is a compound that is very absorptive of both polar and non-polar organic molecules, yet repels water. While absorbing organic matter, its volume expands to up to six times its original size in a process called "swelling" [14, 15]. SOMS's hydrophobicity and swelling ability makes it a great candidate for groundwater treatment through an HDC reaction [16]. Figure 1 below show the chemical make-up of the precursor used in the synthesis of SOMS [14].

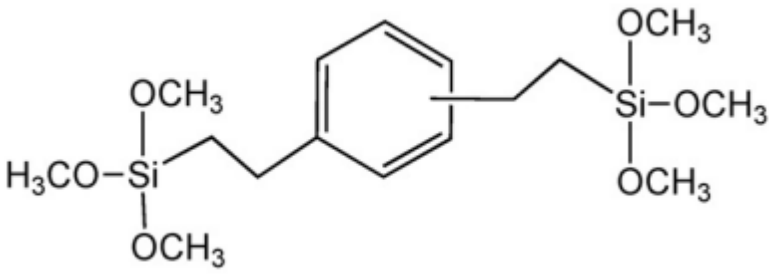


**Figure 1: Precursor for SOMS Synthesis**

Previous tests of liquid HDC of TCE using Pd/SOMS have shown that the reaction is significantly more efficient compared to the standard industry catalyst supports of alumina and activated carbon [17]. Absorption of TCE swelled the support and opened additional catalyst pores, increasing the surface area, pore volumes, and initial concentration of TCE inside the pores, improving reaction kinetics. However, in the gas phase, the pore opening process was not observed, and the SOMS decomposed at the higher temperatures, reducing its swelling ability. Since it still maintained its hydrophobicity after high-temperature treatment, it is important to modify the SOMS so that it can work in high temperature reactions. While the liquid-phase HDC of TCE works successfully, it is important to make the reaction work in the gas-phase as well

[17]. It is possible that the gas-phase HDC technique can replace the incinerator unit in the secondary vapor treatment system, therefore releasing less carbon dioxide. Additionally, the ability to repel water in processes like water treatment can reduce the deactivation of the catalyst by preventing the chloride and sulfide ions in water from getting inside the catalyst support's pores. The combination of SOMS's physical and chemical traits as well as the need for a high-temperature gas-phase solution makes this project both unique and important. Also, the products from the HDC reaction (ethane and hydrochloric acid) are both useful compounds, the former being a natural gas hydrocarbon and the latter being a strong acid used in chemical labs. By creating these economical products rather than the greenhouse gas carbon dioxide, this is a much more sustainable way of treating water than current practices.

# 2. Literature Review

In order to gain a broader understanding of the material being covered, this section will investigate current research in fields relevant to this paper. Such topics will include hydrodechlorination, deactivation of catalysts, and swellable organically modified silica.

## 2.1. Gas-Phase Hydrodechlorination of Trichloroethylene

Another study that analyzed the hydrodechlorination reaction of trichloroethylene in the gas phase is, "Hydrodechlorination of trichloroethylene on noble metal promoted Cu-hydrotalcite-derived catalysts." The study analyzed how preparing the HDC catalysts with hydrotalcites containing copper and magnesium with palladium and platinum metals in order to study whether the alloy created would affect the reaction. The results found that the alloy assisted the reaction kinetics for the $Cu_{0.4}Pt_{0.6}$, but the $Cu_{0.25}Pd_{0.75}$ exhibited a decrease in reaction rate because Cu sites were more prone to chlorine blockage. Although the percentages of each catalyst alloy did not affect the results by much, the different catalysts and hydrotalcites used did affect the results significantly [18]. This study shows the importance of finding optimal catalysts. By combining different metals together, the optimal catalyst can be found. While different supports may also influence which combination is better, such studies can be used to find a more effective catalyst to use on the SOMS or H-SOMS supports that we study in this study.

## 2.2. Deactivation of Catalysts on Alumina

In 2005, Lopez et al. conducted a study called, "Deactivation of a Pd/Al2O3 catalyst used in hydrodechlorination reactions: Influence of the nature of organochlorinated compound and

hydrogen chloride." The study ran the reaction to convert tetrachloroethylene, chlorobenzene, and dichloromethane under a toluene solvent into unchlorinated hydrocarbons in a gas phase reaction. As the reaction occurred, the pattern of deactivation was measured for each compound and each catalyst was analyzed before and after the reaction and deactivation. The study found that both coke formation and HCl were major sources of the catalyst deactivation, especially at lower temperatures. Hydrochloric acid's effect on the catalyst is due to the ionic compound causing the Pd metal to oxidize. Deposits of carbonaceous compounds on the other hand physically block reactants from the catalyst sites, and favors high HCl concentrated conditions and lower temperatures as well. Consequently, should a process wish to recycle unreacted hydrogen, it would be best to remove HCl if feasible. When the three chlorinated compounds were compared, the results showed that the chlorobenzene and dichloromethane had fast initial catalyst deactivation that levelled out as the reaction continued, while the tetrachloroethylene showed deactivation that was more continuous and moderate [13].

Lopez et al.'s study shows the importance of finding methods to protect catalytic sites. Their use of alumina support in the gas phase reaction makes this study very relevant for this paper since the reactions conducted were similar in nature, making the results relatively comparable. Although trichloroethylene was not used, tetrachloroethylene is a similar substitute that has also been studied in previous studies here at The Ohio State University.

## 2.3. Swellable Organically Modified Silica

Since this material is so new, there are only about four papers that discuss it, and all of them are written by its discoverer: Paul Edmiston from the University of Wooster. The material was first written about in 2005 in the paper, "Highly swellable sol–gels prepared by chemical

modification of silanol groups prior to drying." The paper describes the synthesis process of the material and discusses the chemical properties. The SOMS was able to swell up to 6 times its original dried state, depending on the organic solvent used as an adsorbate, however it does adsorb both polar and nonpolar chemicals. The swelling process is also reversible when heat is used to dry the material and remove the organic chemicals. Since the sol-gels used to form the material was hydrophobic, the material would not absorb water at all, making it hydrophobic as well [14]. These findings were what encouraged us to research this material more as a possible catalytic support.

"Organic–Inorganic Hybrid Materials that Rapidly Swell in Non-Polar Liquids: Nanoscale Morphology and Swelling Mechanism," was written two years later and gave more insight on the chemical structure of SOMS. The study found that the organic/inorganic compounds were linked together by carbon chains linked to aromatic functional groups that provided flexible connections to alkoxysilanes that were responsible for the polymerization of the material into a network of silicon and organic groups. Chemical analysis tests suggested that the swelling nature was due to the interparticle interactions of the organosilicate particles that held the network bound until organic solvents could enter the network and break those attractions. The breaking of these bonds allowed the network to expand, which increased the amount of volume with a force of 50 N/g. The paper concluded that SOMS had potential in remediation and chemical sensing [15]. This study provides clearer insight on how the SOMS material operates, which is important when considering the effects of heat treatment.

"Absorption of dissolved organic species from water using organically modified silica that swells," from 2009 tested whether SOMS could effectively draw trichloroethylene, perchloroethylene, methyl t-butyl ether, toluene, naphthalene, acetone, 1,4-dioxane, and 1-

butanol from water. The material was highly effective at removing all organic compounds from the water – even seawater, and exhibited greater capacity than activated carbon – 3 times its dry weight [16]. Such behavior is vital when considering materials to use in wastewater treatment, which is what the hydrodechlorination can hopefully accomplish.

The most recent study is from last year called, “Adsorption of Gas Phase Organic Compounds by Swellable Organically Modified Silica.” The paper sought to discover how effective the compound was at adsorbing organic molecules in the gas phase, since the previous papers focused on the liquid phase. The static adsorption capacity of SOMS was as much as 1.07 grams of organic solvent per gram of SOMS, however coadsorption was utilized to expand this capacity to as much as 5.7 g/g [19]. Since our research was conducted before this study came out, it is possible that the coadsorption technique could be used to make the SOMS material more susceptible to swelling during our reaction. However, it is unlikely that actual water treatment plants will achieve vapor pressures close to saturation. Nonetheless, this paper shows potential for expanding gas-phase hydrodechlorination reaction utilizing SOMS.

# 3. Methodology

This experiment involved four different parts in order to compare H-SOMS to SOMS and $Al_2O_3$ as a catalytic support. These steps include synthesizing H-SOMS, preparing the catalyst, characterizing it using nitrogen physisorption, temperature programmed decomposition, and carbon monoxide chemisorption, and gas-phase HDC of TCE catalytic activity measurements. The details of each are outlined below.

## 3.1. Synthesis of H-SOMS

While alumina with 1% Pd catalyst was purchased commercially from Sigma Aldrich, swellable organically modified silica was obtained from Dr. Paul Edmiston. Synthesis of this compound involved a sol-gel process where 0.144 mole of bis(trimethoxysilylethyl)benzene (BTEB) was dissolved in 220 mL of acetone and 1.5 mL of 1.0M tetrabutylammonium fluoride was dissolved in 7.8 mL of water. The two solutions were mixed and underwent gelation. The product was then allowed to rest at 25ºC for six days before rinsing and filtering with acetone. The resulting gel was crushed and soaked for two days at room temperature in 5% *v*/*v* solution of hexamethyldisilazane in acetone while constantly mixed. Finally, the resulting gel was rinsed with acetone and dried at 110 °C to obtain SOMS as a white solid.

The compound was then saturated with acetone, causing it to swell to maximum size. The enlarged compound was placed in a horizontal quartz tube and flushed with nitrogen gas for five minutes to remove oxygen from the system. The tube containing the material was then shock-heat-treated at 600 °C for two hours with nitrogen gas still flowing over the SOMS. The heat treatment process destroyed the swelling mechanisms, but held the pores open for the catalyst

and organic material to enter. Although the material lost the ability to swell to some extent, it retained its hydrophobic and adsorptive properties.

## 3.2. Catalyst Preparation

Palladium metal was incorporated into the SOMS and H-SOMS catalytic supports through a process called incipient wetness impregnation (IWI) technique. Approximately 2.13% of the support weight of palladium acetate was dissolved in excess acetone in order to achieve a 1 wt% of Pd vs the support batch, which was then added drop-by-drop to the support with vigorous stirring to dry and mix the catalyst well. If the solid became saturated with liquid, the mixture was allowed to dry until more solution could be added. Once the entire solution was mixed in and allowed to dry for 12 hours, $NaBH_4$ solution was used to reduce the Pd metal particles inside the SOMS by filtering and rinsing the mixture with ethanol and distilled water. A 5% $H_2$/He gas mixture reduced the palladium in H-SOMS for one hour at 400 °C. The heat treatment was not performed on the SOMS because the chemical structure would decompose and lose its swelling ability.

## 3.3. Characterization Studies

In order to gain a better understanding of the nature of the supports as well as Pd-incorporated catalysts at the molecular level, three different characterization methods were used. The details of each method are outlined below.

### 3.3.1. Nitrogen Physisorption

In order to measure the surface area, pore size, and pore volumes of each support and catalyst, nitrogen physisorption was utilized. The method takes advantage of the Brunauer-Emmett-Teller (BET) isotherm to find surface area, and the Brunauer-Joyner-Helena (BJH)

isotherm to find the pore volume and diameter. A Micromeritics ASAP 2020 (accelerated surface area and porosimetry) instrument was used to collect the nitrogen adsorption/desorption isotherms for the surface analysis of the catalysts. Samples were degassed at 130°C for 12 hours under a vacuum, and then analyzed at 77K using liquid nitrogen in the analysis port.

### 3.3.2. Temperature Programmed Decomposition

As SOMS is heated and transitions into H-SOMS, it gives off several products that can be analyzed using mass spectroscopy. In order to identify what species were evolved during calcination, the temperature-programmed desorption (TPD) method was used under inert conditions. Using a Carbolite MTF 10/15/130 furnace, SOMS was inserted into a 4 mm-ID quartz reactor with quartz wool. Helium was flowed through the system at a flow rate of 30 ml/min and at room temperature until a consistent mass spectroscopy reading was attained. Then the furnace was heated consistently at 10ºC per minute to 800ºC and was maintained for several hours while the mass spectrometer (MS - MKS-Cirrus II) analyzed the products that were given off.

### 3.3.3. CO Chemisorption

Carbon monoxide was used as a probe molecule to examine the nature of Pd particles in Pd-incorporated catalysts. This method will analyze the amount of CO reacted with Pd on the catalyst. Using the same furnace and mass spectroscopy setup from the TPD experiments with the addition of a carbon monoxide gas line through a six-port valve with a sample loop which has a volume of 0.124 ml, pulses of CO were sent through the samples so that the catalyst could interact with the gas until all active sites have fully reacted. The mass spectrometer measured the amount of CO uptake at each pulse based on a previously calibrated feed. The Pd dispersion was

assumed to be the number of moles of Pd reacted with CO divided by the number of moles of Pd in the sample.

### 3.4. Gas-phase Hydrodechlorination Experiments

For the gas-phase reaction testing, nitrogen was mixed with TCE in a bubbler at 35°C. The exit stream from the bubbler was diluted with nitrogen and mixed with hydrogen so that the feed composition was 0.7% TCE in excess hydrogen at a 1:30 TCE-to-hydrogen molar ratio. The reactant stream was then carried to a 4-mm-i.d. quartz reactor with a quartz frit containing the catalyst, all encased in the resistively heated furnace. The reaction was carried out at 100ºC, 150ºC, and 200ºC with insulated gas lines to prevent condensation and an Omega CSC232 PID temperature controller. The outlet of the reactor was connected to a Shimadzu Scientific 2010 Gas Chromatograph (GC) coupled with Flame Ionization Detector (FID) and Pulsed Discharge Helium Ionization Detector (PDHID) to separate, identify, and quantify the reaction products.

*Pulse chemisorption and temperature programmed decomposition experiments were performed by Hyuntae Sohn. Gas phase activity experiments were performed by Hyunate Sohn and assisted by Trevor Wendt. Nitrogen physisorption experiments were performed by Trevor Wendt.

# 4. Results and Discussion

After following the procedures above, the data from each study was collected for analysis. Such results are shown and explained below.

## 4.1. Characterization results

### 4.1.1. $N_2$ Physisorption

Table 1 shows the surface areas, pore volumes and pore diameters of SOMS, H-SOMS, 1%$Pd/Al_2O_3$, 1% Pd/SOMS, and 1% Pd/H-SOMS from the Nitrogen Physisorption experiments. The H-SOMS surface area increased by about 40% from its original state, while the pore volume doubled and the pore diameter increased by 45%. These results mean that swelling the pores and calcinating the compound successfully opened up the pores and created more surface area for possible catalytic sites. These values also decreased when the Pd was impregnated into the respective supports, which insinuates that the Pd particles likely at least partially filled up pores. The commercial $Pd/Al_2O_3$ had significantly less surface area than any of the other materials and had relatively small pore volume and a noticeably larger pore diameter.

Table 1: Nitrogen Physisorption Results from the Micromeritics ASAP 2020

| | BET Surface Area | Pore Volume | Pore Diameter |
|---|---|---|---|
| SOMS | 493 ($m^2/g$) | 1.03 ($cm^3/g$) | 84 (Å) |
| H-SOMS | 682 ($m^2/g$) | 2.07 ($cm^3/g$) | 122 (Å) |
| 1% $Pd/Al_2O_3$ | 156 ($m^2/g$) | 0.85 ($cm^3/g$) | 217 (Å) |
| 1% Pd/SOMS | 479 ($m^2/g$) | 0.56 ($cm^3/g$) | 47 (Å) |
| 1% Pd/H-SOMS | 546 ($m^2/g$) | 1.09 ($cm^3/g$) | 75 (Å) |

### 4.1.2. Temperature Programmed Decomposition

The results of the mass spectroscopy readings from the temperature programmed decomposition experiment are recorded in figure 2. The temperature was increased to 800ºC and then held constant for two hours, as represented by the black break line. The mass/charge ratios analyzed were 2 ($H_2$), 15 ($CH_4$), 18 ($H_2O$), 28 ($C_2H_6$), 29 ($C_3H_8$), 32($O_2$) and 44($CO_2$) because the ion fragmentation of these compounds needed to be considered so that their values did not contribute to other fragments. As the trends in the graph shows, most readings exhibit an increase in intensity at 500ºC. This increasing trend means that the chemical structure of the SOMS began to decompose around that temperature. Since methane and ethane are the two most abundant hydrocarbon products, the C-C bonds in the aromatic rings of SOMS were likely breaking. The intensities also decreased after 800ºC had been reached. It is likely that this behavior was because any gases that were formed had already been exhausted, so fewer products were being given off.

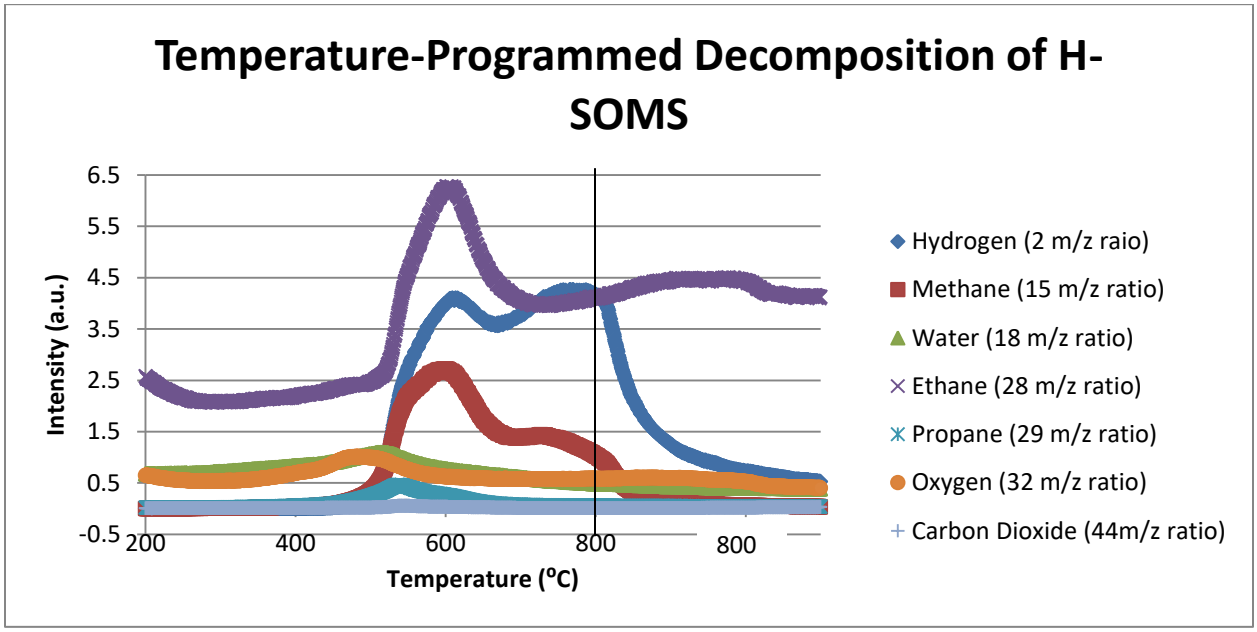


**Figure 2: TPD of H-SOMS at Constant Temperature Increase Until 800 Degrees Celsius**

Since oxygen was removed from the environment inside the tube, little oxidation could occur. Preventing combustion allowed the carbon structure of SOMS to stay somewhat intact. Therefore, the carbon dioxide produced remained relatively close to zero throughout the whole experiment, with the exception of a few surface oxygens in the material's chemical structure being released at 500ºC.

### 4.1.3. CO chemisorption

As CO was sent through each catalyst, the mass spectroscopy measured how much CO was not reacted with the catalytic active sites. The results from the study are shown in figure 3. For the first pulse, alumina and H-SOMS showed less than 100% of carbon monoxide made it through to the mass spectrometer without being adsorbed by the material. However, 1% Pd/SOMS did not adsorb any carbon monoxide at all. These results signify that the catalytic sites on SOMS were deposited inside the matrix of SOMS, thus completely protected, while CO reacted with Pd molecules present on 1% Pd/H-SOMS and 1% Pd/alumina. One reason why SOMS behaved the way it did could be because it was in an unswollen state, so the pores were closed off, protecting the Pd sites. It is also notable that the initial 1% Pd/H-SOMS pulse did not consume as much CO as the 1% Pd/alumina, which means that the H-SOMS protected its active sites better than alumina. Better protection could signify that the support may protect against poisoning better. Yet the heat treatment did increase the Pd interactions with CO. As more pulses of carbon monoxide were sent to the catalyst bed, no more CO could react with each catalyst, so the mass spectroscopy readings showed the full amount of CO passing through.

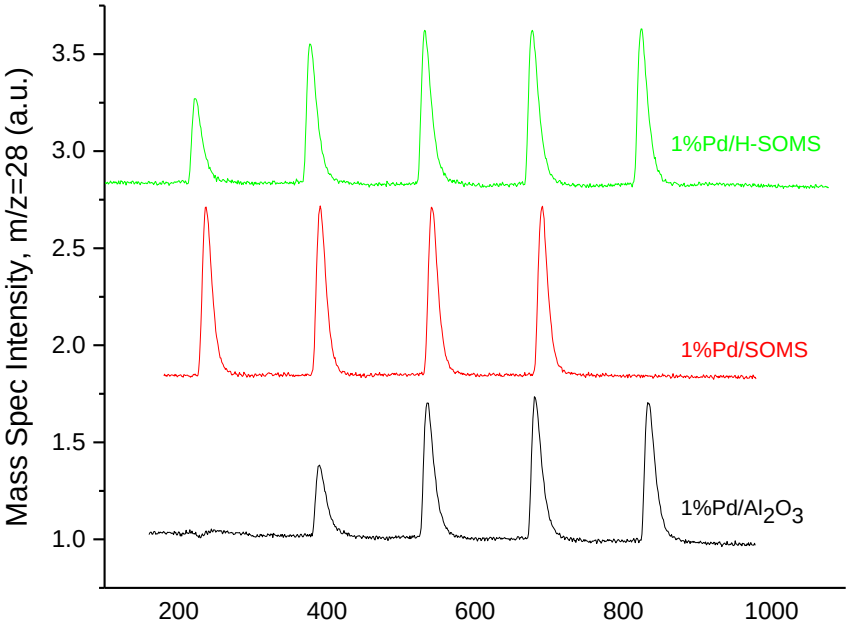


**Figure 3: CO Chemisorption Pulses for the Catalysts of Interest**

## 4.2. Gas-Phase Activity Results

During the gas-phase hydrodechlorination reactions in the flow reactor, the three different catalysts were compared at four different temperatures. The exhaust stream from the reactor was flowed through the GC where separation, detection, and quantification of reaction products and unconverted feed were performed. Figure 4 shows the amount of reactant left in the stream as a percentage of the original amount sent through the reactor. Across the board, higher temperatures led to higher reaction rates, although it was important not to go higher than 200ºC or else the SOMS material would lose its swelling ability. At high temperatures, the reaction had more energy to react, and therefore achieved higher conversions.

It is also important to note that as expected, regular SOMS had the lowest reactivity from the experiment, likely since there was not enough concentration of organic materials to swell the support effectively to open up the pores and give access to the catalytic palladium sites. H-SOMS performed significantly better than its unheated counterpart performed, but fell short of

the conversions alumina was able to achieve. Although, at 200ºC, H-SOMS and alumina's conversions were similar at over 90% conversion.

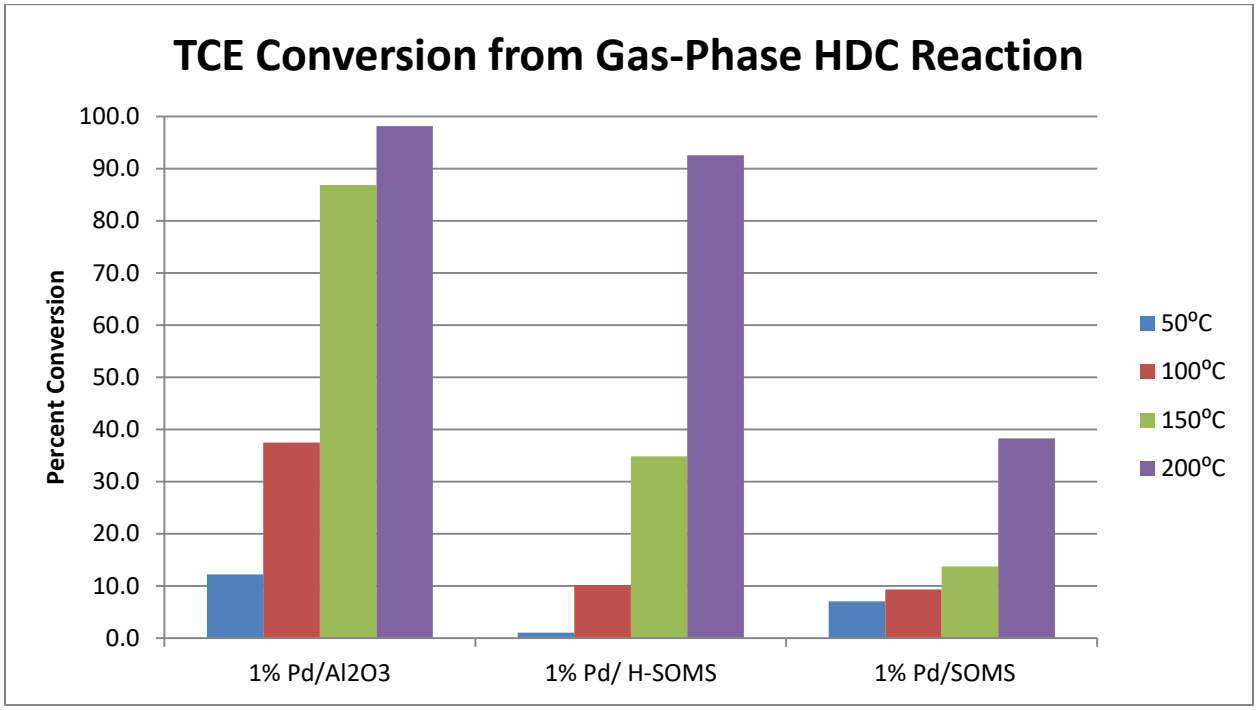


**Figure 4: TCE Conversion in HDC Reaction**

Another metric to measure the success of each catalytic support was to look at the various major and side products. The primary product of the reaction was hydrochloric acid and ethane, so the percent yield of ethane was able to be recorded in the GC and was graphed in figure 5 below. Since some bi-products were given off, the ethane yield values were lower than the amount of TCE converted. However, the general trends seen in the conversion measurements from figure 4 directly agree with the ethane readings: increasing temperature increases the amount of product produced, and 1% Pd/alumina had higher yields while 1% Pd/SOMS had lower yields and 1% Pd/H-SOMS struck a balance between the other two catalysts.

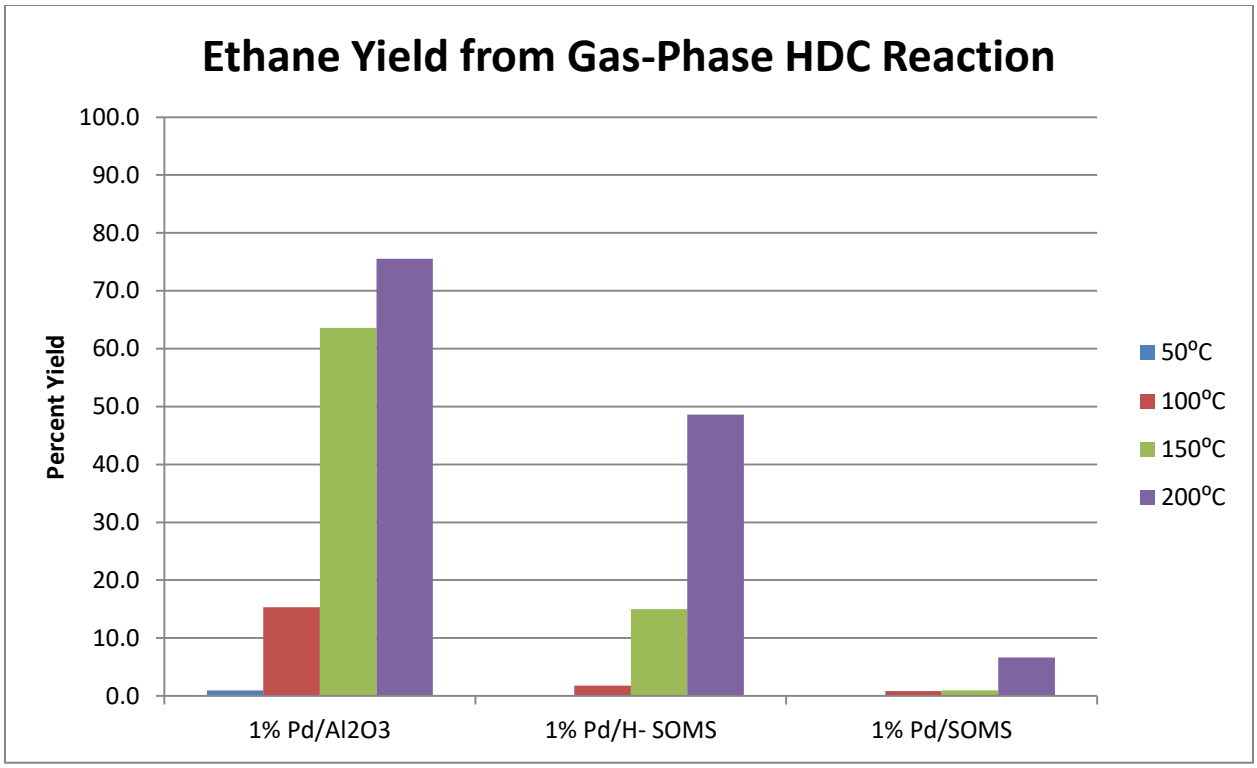


**Figure 5: Yield of Ethane from HDC Reaction**

The reaction also contained numerous bi-products from the reactions. Distributions of the total products for each of the supports at 200ºC are in figure 6 below. SOMS had a relatively large amount of bi-products, since only 18% of the total product was ethane. However, H-SOMS and alumina had much better selectivity of the desired product.

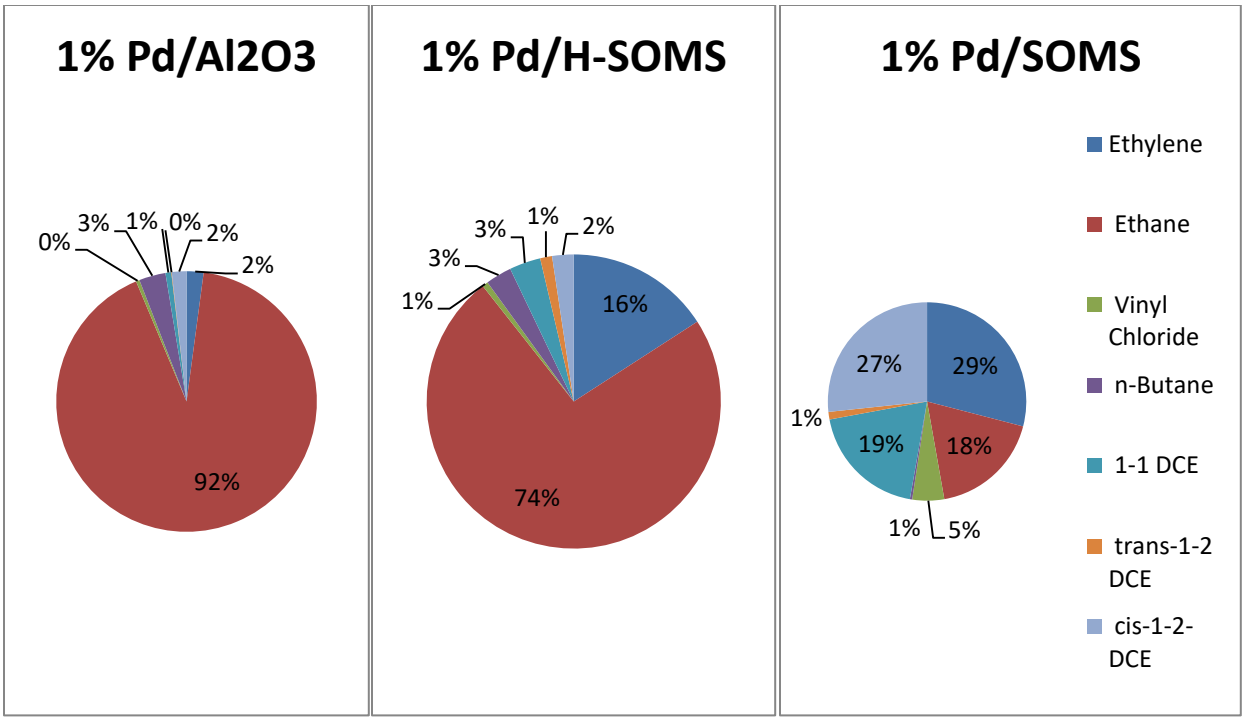


**Figure 6: Product Distribution from HDC Reactions at 200°C**

Therefore, SOMS proved to be kinetically undesirable for the gas-phase reaction in each of these three ways of analyzing the HDC reaction. However, it should be noted that the material has proven to be even more effective than alumina support for the liquid phase reaction since the more concentrated organic material can swell the material and cause its pores to open up [17]. However, the gas phase is not concentrated enough to cause the same swelling conditions for SOMS to operate the same way. SOMS is also important to still consider due to the protection is provides to the catalytic sites, which could be helpful when poisons could be involved. Since H-SOMS was pre-swollen and then petrified, its pores were already opened and allowed access to the Pd sites within the pores, providing much more competitive reaction results.

# 5. Conclusions and Recommendations

This study analyzed three different materials as catalytic supports for a hydrodechlorination reaction of trichloroethylene using palladium catalyst: commercial alumina, swellable organically modified silica, and heat-treated SOMS. The characteristics of each material were measured using nitrogen physisorption, temperature-programmed desorption, and carbon monoxide chemisorption. Then each catalyst was used in a continuous gas-phase reactor that converted TCE under hydrogen into ethane and hydrochloric acid, and the outgoing stream was measured by a gas chromatography unit.

By treating SOMS with high temperatures while in its swollen state, the material lost the ability to retract in size, immobilizing its pores in an open state. During the heating process, the TPD analysis found that the structure began to decompose around 500ºC and released methane and ethane and hydrogen. The products likely came from the breaking down of the aromatic structures inside SOMS. CO chemisorption experiments found that the SOMS material completely protected the catalytic sites from adsorption, while H-SOMS and alumina had open pores that allowed carbon monoxide to adhere. The Pd particles were not totally in the matrix – some were on the surface, which increases the intrinsic kinetics. The high-temperature treatment also allowed the H-SOMS to achieve the highest surface area and pore volume compared to alumina and SOMS. Although impregnating the catalyst on each support decreased their respective surface areas and volumes, the 1% Pd/H-SOMS still had higher values than the other catalysts.

The high surface area allowed 1% Pd/H-SOMS to achieve higher conversions during the flow reaction than 1% Pd/SOMS, although 1% Pd/$Al_2O_3$ had the highest overall conversion. Since H-SOMS had larger pores, it is likely that the catalytic sites were slightly less accessible

due to their location inside pore cavities inside the structure. These traits are desirable when poisons are of concern rather than solely conversion percentages, since protecting catalytic sites can extend the life of a catalyst bed.

More research needs to be done to investigate the properties of H-SOMS. The experiments from this study do not provide a very good image of the changing chemical structure during the heating process. Methods like infrared spectroscopy, high angle annular dark field scanning transmission electron microscopy, nuclear magnetic resonance spectroscopy, and x-ray absorption near edge structure spectroscopy would provide clearer methods of understanding the material being analyzed. It is also important to note that since the conditions for this reaction typically involve moisture and poisons that would degrade the catalyst, each catalyst should be compared under these conditions. Such analysis would give better insight to the best catalyst support to use in the gas phase in a realistic application.

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